# FISCHER-TROPSCH SLURRY CATALYSTS FOR SELECTIVE TRANSPORTATION FUEL PRODUCTION

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#### Introduction

The future use of coal as a source of conventional transportation fuel will depend on the development of an economical and energy efficient liquefaction process. Technologies that have been commercially proven or that are close to commercialization include the fixed—and fluidized-bed Fischer-Tropsch (FT) synthesis, methanol synthesis (fixed-bed and slurry-phase) and the Mobil methanol—to-gasoline process. Of these technologies, the Fischer-Tropsch hydrocarbon synthesis produces the widest slate of products and has been in operation for the longest period.

The FT reaction produces hydrocarbons with a broad spectrum of molecular weights ranging from methane to paraffin waxes. This broad product distribution significantly limits the maximum yield of transportation fuel fraction and creates the need for further downstream processing such as hydrocracking and light olefin oligomerization to increase such yields. Research has shown that selectivity is controlled mainly by catalyst composition and process conditions. In order to improve the economics of the FT process, a catalyst should display high activity and minimize the formation of both light hydrocarbons  $(C_1-C_4)$  and waxes  $(C_2+1)$ , while producing the bulk of the product fraction in either the gasoline  $(C_5-C_{11})$  or dies  $(C_{12}-C_{18})$  ranges. Product selectivity, however, has been more successfully controlled by manipulating process conditions. Since the FT reaction is exothermic, control of the reaction heat plays a major role in controlling product selectivity. The slurry-phase process offers the best recent of both reactions. The slurry-phase process offers the best means of heat transfer and temperature control and has been shown to improve liquid product selectivity mainly by lowering the light gas yield(1). The amount of data from slurry-phase operation, however, is limited to only a few studies and significant differences have been reported in yields, catalyst life and ease of operation(1-4). More research is needed to fully determine the potential of slurry-phase FT processing, and we will describe our efforts in developing new slurry-phase FT catalyst systems.

Under an earlier contract with the Department of Energy, Air Products and Chemicals, Inc. developed several new slurry-phase FT catalysts that enhanced selectivity to liquid fuel products(5). One group of catalysts included supported metal carbonyl clusters modified by promoters. To further develop and improve these catalyst systems, Air Products has begun a program to thoroughly investigate the preparation, characterization and performance of metal carbonyl cluster-based catalysts for use in slurry phase FT technology. Our overall objectives focused predominately on increasing catalyst activity, improving product selectivity for liquid fuels, reducing the yield of methane, developing catalyst systems active at high CO/H, ratios and incorporating water-gas shift activity. Catalysts were evaluated by a combination of tests in stirred and fixed-bed reactors. In addition, catalysts were characterized by surface techniques and bulk analyses.

#### Experimental

<u>Catalyst Preparation</u>: Catalyst precursors and supports were purchased from commercial sources. The following supports were used after a calcining treatment at  $500^{\circ}$ C for 3 hr in air:  $\gamma$  -Al<sub>2</sub>O<sub>3</sub> (Catapal<sup>©</sup> SB, 217 m<sup>2</sup>/g), SiO<sub>2</sub> (Davison 952, 339

 $m^2/g$ ), MgO 3.6 SiO<sub>2</sub> (Florisil®, 298  $m^2/g$ ) and TiO<sub>2</sub> (Degussa P-25, 50  $m^2/g$ ). The catalysts and precursors were protected from air and moisture using standard Schlenk techniques (6) and a Vacuum Atmospheres dry box. All solvents were reagent grade and distilled from sodium benzophenone ketyl in a nitrogen atmosphere. Immediately prior to use, the supports were further dried in vacuo at 110°C for 1-2 hr. Catalysts were prepared by impregnation (to incipient wetness) of the supports with separate solutions containing the promoter and metal carbonyl. Several promoters were evaluated, with one being particularly effective. All catalysts discussed in this report made use of this promoter (designated "Prom"). This method was used for the following catalysts that were prepared from metal carbonyls:

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• 3.8% Co/6.8% Prom on Al<sub>2</sub>O<sub>3</sub>

• 2.8% Ru/4.9% Prom on Al<sub>2</sub>O<sub>3</sub>

• 4.7 Co on Al<sub>2</sub>O<sub>3</sub> (no promoter)

• 5.1% Co/4.4% Prom on Al<sub>2</sub>O<sub>3</sub>

• 4.0% Co/6.4% Prom on Al<sub>2</sub>O<sub>3</sub>

• 10.8% Co/8.5% Prom on Al<sub>2</sub>O<sub>3</sub>

• 3.5% Co/6.6% Prom on SiO<sub>2</sub>

• 3.7% Co/7.2% Prom on MgO 3.6 SiO<sub>2</sub>
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Two catalysts were also prepared using  $\mathrm{Co(NO_3)_2}$  as the cobalt source. The method was slightly modified, in that after addition of the promoter and removal of the solvent, the material was exposed to air. An aqueous solution of  $\mathrm{Co(NO_3)_2}$  was then used to impregnate the support, the material was dried at  $10^{\circ}\mathrm{C}$  and  $\mathrm{calcined}$  at  $300^{\circ}\mathrm{C}$  in air for 5-6 hr. The two catalysts and their analyses are a follows:

• 4.2% Co/7.1% Prom on  $\gamma \sim Al_2O_3$ • 4.6% Co/7.5% Prom on SiO<sub>2</sub>

• 3.5% Co on TiO, (no promoter)

Gas Phase Tests: Prior to slurry-phase testing, gas-phase tests were conducted to screen catalyst activity. Those catalysts with gas-phase activities greater than 20 mol of syngas converted/kg of catalyst/hr were selected for further slurry-phase testing.

The gas phase reactor was a fixed-bed, 316 SS tubular unit with downflow configuration and 10 cc bed volume. All gas-phase tests used a CO/ $\rm H_2$  feed ratio of 1 at 300 psig and nearly all were conducted at 1000 GHSV ( $\rm v/v$ ). Temperature was varied in the range of 220 to 280°C. For the gas-phase tests, the catalyst was activated with  $\rm H_2$ .

<u>Slurry Phase Tests</u>: Two continuous, stirred, 1 liter autoclave reactors were used for slurry tests. Figure 1 shows a schematic diagram of one of these units. For the slurry phase tests, catalysts were activated in a separate, 150 cc fixed bed tubular unit using either pure  $H_2$  or 20% syngas in  $N_2$ . Activated catalyst was slurried in deoxygenated paraffin oil (Fisher #0-122) in the dry box and transferred to the slurry autoclave reactor under a  $N_2$  blanket.

Slurry tests were performed continuously for up to 21 days, except for the test of basecase Co on promoted alumina, which was run for 55 days. Inlet CO/H<sub>2</sub> ratios were 2, 1.5, and 0.5, with emphasis on CO-rich feeds. Space velocities were 1 and 2 NL/g of catalyst/hr. Operating pressures and temperatures ranged from 300 to 600 psig and 220 to 280°C, respectively. The solids content of the slurry was 15 to 25 wt%.

Because of the complexity of the Fischer-Tropsch product, equilibration of the reactor and the product collection systems, and a flexible quantitative analysis scheme incorporating all products including waxes were required to produce good carbon and hydrogen material balances, which were in the range of 95-105%. The details of the analytical and data handling system have been published(7). The method, illustrated schematically in Figure 2, consisted of four separate gas

chromatographs linked via a Perkin-Elmer Sigma 15 computing integrator/controller to a Tektronix 4052 microcomputer equipped with a 1.9-megabyte disk system.

<u>Catalyst Characterization</u>: Catalyst supports were characterized by B.E.T. surface area measurements, mercury intrusion porosimetry, helium pycnometry, and particle size distribution. Freshly prepared catalysts and reduced catalysts were characterized by B.E.T. surface area measurements and hydrogen chemisorption. Metal loadings were determined in-house and at Schwarzkopf Microanalytical Laboratories. Some of the catalysts were also studied using X-ray photoelectron spectroscopy and X-ray diffraction.

#### Results and Discussion

The type of activation used for "conventional" FT catalysts has been shown by several researchers to affect performance(8). Dry detailed the effects of activation on the performance of precipitated and fused iron catalysts(9) and indicated that pure  $\rm H_2$  was preferred. Another recent study of catalyst performance vs. degree of reduction for  $\rm Co(NO_3)_2$  on alumina used only  $\rm H_2$  reduction(10). The activation of supported metal carbonyl catalysts has generally been done by thermal decomposition under vacuum or inert atmosphere(11). The effect of reducing gases such as  $\rm H_2$  and syngas on supported metal carbonyls has not been well established, but these gases should improve the degree of metal reduction since the metals are initially oxidized by the support.

Our study of activation conditions compared pure  $\rm H_2$  activation with syngas (CO/ $\rm H_2$  = 1) activation using the 4% Co on promoted alumina catalyst. Hydrogen activation significantly improved both activity and liquid fuel selectivity in the slurry tests. Figure 3 compares syngas conversion following both types of activation as a function of temperature and space velocity. At comparable reaction conditions,  $\rm H_2$  activation converted 30 to 40% more syngas in the 220 to 260°C range, but at 280°C, the difference was less. For  $\rm H_2$ —activated catalyst at lower space velocity, the syngas conversion appeared to be independent of temperature between 240 and 280°C.

Table 1 shows that  $\rm H_2$  activation increased the  $\rm C_{E-23}$  selectivity by 25 relative percent, from 57 to 71 wt% and decreased both the  $\rm CH_4$  and wax selectivity. The increased activity probably resulted from a higher degree of Co reduction but the reason for the enhanced liquid fuel selectivity is less clear. Perhaps the degree of reduction and metal particle sizes which both depend on activition conditions together affect chain growth probability. However, we did not examine or compare the catalysts from different activation procedures for these two properties. Since a major objective of our research was to study the use of metal carbonyls as catalyst

Table 1. Effect of syngas vs. hydrogen activation on hydrocarbon selectivity.

4% Co ON PROMOTED - ALOD.

	SYNGAS	H <sub>2</sub>
SPACE VELOCITY, NL/g cat/hr.	1.6	2.0
CO/H <sub>2</sub>	1.6	1.6
PRESSURE, PBIG	300	300
TEMPERATURE, *C	250	256
WT%		
<u>c,</u>	11.5	7.2
C2-4	10.4	10.6
C8-11	29.2	34.1
C12-18	15.3	27.9
C19-23	12.5	0.5
C24+	21.1	11.4
C <sub>5-23</sub>	87.0	70.8

precursors, a comparison to conventionally prepared catalysts was necessary. This was done by examining catalysts prepared from cobalt nitrate using the same support and promoter as the cobalt carbonyl-based catalysts. The activity and selectivity of the two catalysts in the slurry-phase reactor are compared in Table 2. Both

catalysts had similar cobalt and promoter loadings. Again, performance differences were larger at lower temperatures. At 240°C, bulk activity of the carbonyl catalyst was more than twice that of the nitrate catalyst, while specific activity was three times higher. At 260°C, the carbonyl catalyst still outperformed the nitrate catalyst in both bulk activity (29% increase) and specific activity (52% increase). The carbonyl-prepared catalyst also provided better liquid fuel selectivity at both temperatures, producing less methane but more light hydrocarbons ( $\mathbf{C}_{2.4}$ ). The major difference was in the production of heavier hydrocarbons, with the nitrate-derived catalyst giving significantly higher  $\mathbf{C}_{24}$ + selectivity. These differences are likely related to metal particle sizes and work is in progress toward characterizing and comparing these catalysts.

Table 2. Effect of Co source on activity and selectivity. 4% Co ON PROMOTED Al<sub>2</sub> O<sub>3</sub> (CO/H<sub>2</sub> = 1.0, 2.0 NL/hr·g cat, 300 paig)

COBALT SOURCE	CARE			N'TRATE		
	240°C	260°C	240°C	260°C		
BULK ACTIVITY, moi SYNGAS/kg cat/hr	35.3	38.5	15.8	29.9		
SPECIFIC ACTIVITY, mol CO/mol Co/min	0.29	0.32	0.09	0.21		
SELECTIVITY, WT%						
<del>c</del> ,	7.9	10.4	10.9	16.5		
C2.4	13.7	15.0	6.5	11.1		
C5-11	37.0	44.5	12.9	26.5		
C12-18	23.4	25.8	19.6	23.8		
C19.23	8.9	2.0	21.9	10.6		
C24+	9.1	2.3	28.0	11.5		
TOTAL FUELS C5.23	69.3	72.3	54.6	60.9		

Several other parameters were examined using the carbonyl-based catalysts. The effect of cobalt to promoter ratio on activity was examined with alumina-supported catalysts. Figure 4 plots specific activity vs. cobalt/promoter ratio for slurry-phase tests at similar reaction conditions and different activation procedures. Catalyst that had undergone syngas activation showed a decrease in specific activity as the Co/promoter ratio increased. The specific activity of the  $H_2$ -activated catalyst, however, was independent of this ratio. One possible explanation involves the interaction of cobalt with the support and its subsequent reducibility. As the amount of promoter decreases, the cobalt interacts more strongly with the support and becomes more difficult to reduce. This decreased reducibility is especially evident when the catalyst is activated with syngas; the cobalt is not sufficiently reduced, resulting in lower activity. Hydrogen, on the other hand, provides sufficient reducing power to activate cobalt that is more strongly associated with the support.

The effect of cobalt loading on bulk activity of the cobalt carbonyl-promoted alumina catalyst was examined in the slurry reactor at 240 and 260°C (Figure 5). Higher loading gave lower bulk activities at both temperatures. Since the catalyst having the higher cobalt loading also had a higher metal dispersion, these results agree with the general trend of increasing activity with decreasing dispersion reported in the literature.

The type of support also had a major influence on catalyst activity, as shown in Figure 6. These catalysts all had similar cobalt and promoter loadings, except for the TiO<sub>2</sub>-supported catalyst, which had no promoter. The silica-supported catalyst was approximately twice as active as all the others. This may be due to the low reactivity between cobalt carbonyl and silica as opposed to the high reactivity of the other supports towards metal carbonyls. A surface area effect is being checked by using a lower surface area silica.

We also studied the effects of operating parameters such as temperature and  ${\rm CO/H_2}$  feed ratio on catalyst performance. As expected, increasing the reaction temperature increased the bulk activity of both  ${\rm Al_2O_3-}$  and  ${\rm SiO_2-}$  supported Co catalysts, as shown

in Figure 7. The  ${\rm SiO_2}$ -supported catalyst activity was independent of temperature at 240°C and 260°C, but increased at 280°C. The activity of the  ${\rm Al}_2{\rm O}_3$ -supported catalyst began to level off at higher temperatures.

The ratio of carbon monoxide to hydrogen in the feed strongly affected catalyst activity, as shown in Figure 8 for promoted cobalt on silica. The catalyst performed best with  $H_2$ -rich feed; when the feed was stoichiometric with respect to hydrocarbon (-CH<sub>2</sub>-) formation (CO/H<sub>2</sub> = 0.5), the syngas converison was highest at 60%. Conversion dropped dramatically to only 25% when the CO/H<sub>2</sub> ratio was increased to 1.5.

This poor performance with CO-rich feeds reflects the low activity for the water-gas shift reaction. Figure 9 further illustrates this by comparing  ${\rm CO/H_2}$  usage ratios with feed ratios for the supported cobalt and ruthenium catalysts, as well as, a precipitated iron catalyst, all in the slurry reactor. The cobalt catalyst showed the poorest CO usage at all feed levels, usage ratios never exceeded 0.60. The ruthenium catalyst offered some improvement with a usage ratio nearly matched to a  ${\rm CO/H_2}$  feed ratio of 1.0. The usage ratio, however, never improved above 1.0 as the feed ratio was increased. The slight improvement in shift activity for ruthenium correlates with its observed shift activity in homogeneous systems(12). Neither catalyst showed the excellent shift activity that is exhibited by precipitated or fused iron catalysts.

In an effort to improve the shift activity of the promoted Co on alumina catalyst, a commercially available, low temperature shift catalyst  $(\text{Cu}/\text{Zn}/\text{Al}_2\text{O}_3)$  was physically mixed with it and tested in the gas phase reactor. The results are summarized in Table 3 along with results in which no shift catalyst was added. The added shift catalyst caused a drop in activity with no indication of enhanced shift activity. There was an increase in oxygenate production, especially of ethanol and higher alcohols. A second gas-phase test of the mixed catalysts, this time using preactivated shift catalyst, still gave lower activity than without shift catalyst, but shift activity increased slightly. Upon increasing the feed ratio from 1.0 to 1.9, however, shift activity declined as the usage ratio dropped to 0.35.

Table 3. Addition of Cu/Zn/Al water-gas shift catalyst to Co/Prom/Al<sub>2</sub>O<sub>3</sub> FT catalyst.

Cetalyst <sup>(1)</sup>	CO/H <sub>2</sub>	Usage Ratio (CO/H <sub>2</sub> )	% Conversion, CO + H <sub>2</sub>	Bulk Activity, (mol syngss/kg cat/hr)
90% F-T 10% SHIFT	1.0	0.53	36	16.8
90% F-T + 10% SHIFT	1.0	0.66	44	21.6
(Preactivated)	1.9	0.36	16	8.6
F-T	1.0	0.59	56	27.0
(I) CONDITIONS	: 240°C,	JUU PEIG, 1	IDOO GMSA	

Another important objective of this study was catalyst characterization and its correlation to catalyst performance. X-ray photoelectron spectroscopy (XPS) was used to examine cobalt oxidation states; three spectra are shown in Figure 10. The lower spectrum is that for oxidized Co on promoted  $Al_2O_3$  prepared from  $CO(NO_3)_2$ . The binding energy for Co 2p electrons of 781 eV cofresponds to established values for CO(II) and CO(III). The strong interaction of cobalt with alumina was evident from the XPS data on fresh catalyst prepared from zero-oxidation-state  $CO_2(CO)_3$ . This data, shown as the middle spectrum, indicates that most of the cobalt is oxidized to 2+ and 3+. Only a shoulder corresponding to a binding energy less than 780 eV suggests the presence of a small amount of zero valent cobalt. Finally, upon activation in pure  $H_2$  at 300°C, the top spectrum was obtained, indicating the presence of a only oxidized cobalt. This is further evidence for a strong

metal-support interaction. That supported cobalt is difficult to reduce, especially at low loadings, is well established(10). Hall and coworkers have used XPS to show that after  $\rm H_2$  reduction at 250°C, alumina-supported  $\rm Co_4(CO)_{12}$  had only 25% of its cobalt as zero valence(13).

Hydrogen chemisorption was used to determine active cobalt surface area and percent dispersion. These results, presented in Table 4, are consistent with the XPS data, showing only small amounts of metallic cobalt. Hydrogen chemisorption was low, especially at room temperature and low loadings. This activated adsorption has been reported by Reuel and Bartholomew(14) and is possibly due to some metal support

Table 4. Catalyst properties.

Catalyel	B.E.T. Burtace Ares	Totel H <sub>2</sub> Uptake	Active Metel Surface Area	N Dispersion
4% Co/Prom/At <sub>2</sub> D <sub>3</sub>	209 m <sup>2</sup> /g	5.0 μmol/g e1 35°C	0.4 m <sup>2</sup> /g	1.2 9.7 10
10.8% Co / Prom / Al <sub>2</sub> O <sub>3</sub>	N.A.	101.2 at 100°C	5.4 3.0	
3.5% Co/Prom/SIO2	316	39.8 at 100°C		
3% Co/8IO <sub>2</sub> <sup>(1)</sup>	N.A.	20	N,A.	11
3% Co/Al <sub>2</sub> O <sub>3</sub> <sup>(1)</sup>	N.A.	5.6	N.A.	10
32% Co/0.6% Ru/Th/Al <sub>2</sub> O <sub>3</sub> <sup>(?</sup>	150-225	150-200	N.A.	N.A.
<sup>[1]</sup> C. H. Bartholomew (1965)	(2) U.S. Patent	4.413.064 to Out	(3.1/.1/83).	

interaction. Comparison shows our data are consistent with those of Bartholomew. Furthermore, a 22% Co/0.5% Ru/Th/Al $_2$ O $_3$  catalyst described in a U.S. Patent to Gulf showed high H $_2$  chemisorption, probably because reduction occurs more readily as metal loading is increased.

Finally, we compared the activity of our supported cobalt catalysts with other supported cobalt catalysts (see Table 5). All of the data, except one, are from fixed-bed reactors. Our bulk activities fall near that of the Gulf catalyst, but are somewhat lower than that of the Shell catalyst. Note though that our data were not obtained at the optimum  $\rm H_2/CO$  feed ratio of 2.0, at which the other catalysts were tested. Turnover frequencies, based on  $\rm H_2$  chemisorption data, are quite good for our catalysts.

Table 5. Catalyst activity comparisons, fixed-bed reactors.

Catelyat	Temp. (°C)	Press. (peig)	Feed H <sub>2</sub> /CO	Bulk Activity (mol syngas/ kg cet/hr)	Frequency (molecules CO x 10 <sup>3</sup> site-sec)
3.5% Co/Prom/BIO <sub>2</sub>	220	300	1.0	31	50
3.5% Co / Prom / SIO 2 (Sluffy)	240	300	1.0	36	41
10.8% Co/Prom/Al <sub>2</sub> O <sub>2</sub>	220	300	1.0	18	14
17% Co/Zr/8IO <sub>2</sub> (Shell)	220	300	2.0	91	M.D.
22% Co/0.6% Ru/Th/Al <sub>2</sub> O <sub>3</sub> (Guff)	215	15	2.0	34	
3% Co/BIO <sub>2</sub> (Bartholomew)	225	15	2.0	N.D.	6

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FIGURE 1

### CONTINUOUS, AUTOMATED FISCHER-TROPSCH SLURRY REACTOR

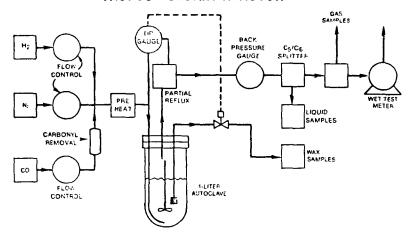


FIGURE 2

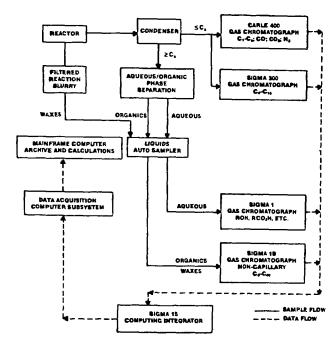


FIGURE 3

# EFFECT OF SYNGAS VS. HYDROGEN ACTIVATION ON OVERALL CONVERSION

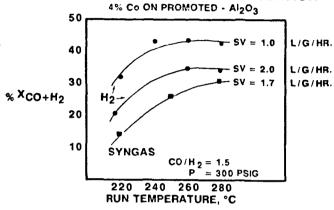


FIGURE 4

## Co/PROMOTER RATIO EFFECT ON ACTIVITY Co ON PROMOTED - AI2O3

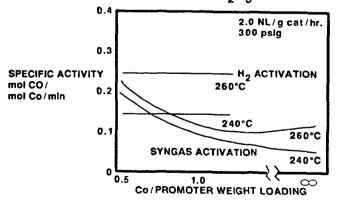


FIGURE 5

# EFFECT OF COBALT LOADING ON BULK ACTIVITY

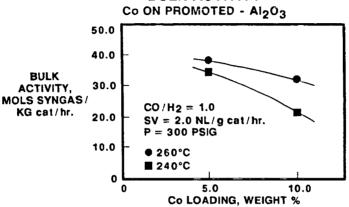


FIGURE 6

# EFFECT OF SUPPORT ON ACTIVITY

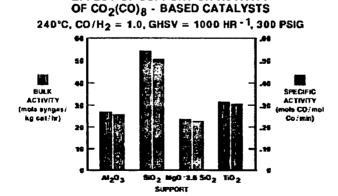
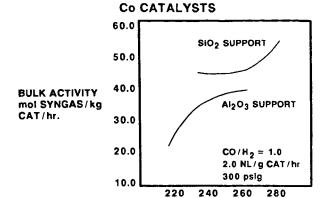


FIGURE 7



**BULK ACTIVITY DEPENDENCY ON TEMPERATURE** 

FIGURE 8

# CONVERSION DEPENDENCY ON CO / H<sub>2</sub> FEED 3.5% Co ON PROMOTED - SiO<sub>2</sub>

TEMPERATURE, °C

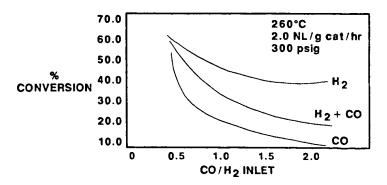


FIGURE 9

### **WATER - GAS SHIFT ACTIVITY**

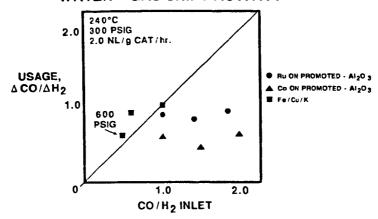


FIGURE 10

### X-RAY PHOTOELECTRON SPECTRA OF:

